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Kinetics and Mechanism of Oxidation of D(+)-Sorbose by Chloramine-T

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The kinetics of oxidation of D(+)-sorbose by chloramine-T has been investigated in high alkaline media. The reaction shows a brief induction period after which a first order dependence in both chloramine-T and substrate is followed. The order in hydroxide ion is observed as fractional being 1.3 under the experimental conditions. The values of energy of activation, frequency factor and entropy of activation have been computed as 28.2 kcal mol^{-1}, 2.90×10^{19} l mol^{-1} s^{-1} and +29.8 e.u. respectively. A plausible mechanism consistent to the experimental result is proposed.

Reducing sugars have been oxidised using several oxidants. The most common oxidants used have been halogens and mainly bromine water. The earlier work on these investigations has been reviewed by Green[1] and Shafizadeh.[2] Isbell and co-workers[3,4] have investigated the oxidation of several reducing sugars by bromine and concluded that β-form of the sugar was more reactive than α-form. The kinetics of oxidation of several sugars (aldoses and ketoses) by chromium (VI),[5] peroxydisulphate[6] were investigated. Ghosh and co-workers[7] studied the kinetics and mechanism of oxidation of various reducing sugars by ammoniacal silver nitrate. The reactions were found to be first order dependent on silver nitrate and independent to the reducing substrate and a suitable mechanism was suggested. Recently Mushran and co-workers[8,9] have investigated the kinetics and mechanism of oxidation of various aldoses (*viz.* xylose, arabinose, ribose, mannose, and galactose) by chloramine-T in high alkaline media.

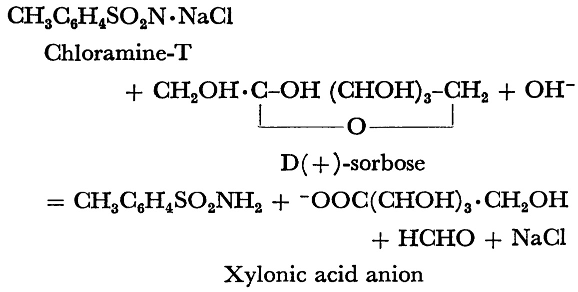
It was observed that the oxidation of ketose *viz.* D(+)-sorbose by chloramine-T takes place only in highly alkaline media. In this communication, the study of the kinetics of oxidation of D(+)-sorbose by chloramine-T is made and a suitable mechanism is suggested.

Experimental

Aqueous solution of D(+)-sorbose (AR, B.D.H. sample) was always freshly prepared. Stock solutions of chloramine-T, osmium (VIII) and sodium hydroxide were prepared as mentioned earlier.[10] All other chemicals used were of analytical grade. Double-distilled water was always used for preparation and dilution of the solutions. The reactions were carried out in outside blackened Jena glass bottles to avoid any photochemical influences.

The alkali sugar mixture was allowed to equilibrate for exactly 45 min after which chloramine-T was added to start the reaction. The kinetics was followed by estimating chloramine-T iodometrically in aliquot portion of the reaction mixture withdrawn in different interval of time.

Stoichiometry. Reaction mixture containing excess of chloramine-T over sorbose were allowed to equilibrate at 50 °C in respective sodium hydroxide concentration. The results showed that 1 mol of sorbose was oxidised by 1 mol of chloramine-T to the aldonic acid of lesser one carbon atom than the parent ketose and thus the stoichiometric equation may be represented as follows:



$CH_3C_6H_4SO_2N\cdot NaCl$
Chloramine-T
$+ CH_2OH\cdot\underbrace{C\text{-}OH\,(CHOH)_3\text{-}CH_2}_{O} + OH^-$
D(+)-sorbose
$= CH_3C_6H_4SO_2NH_2 + {}^{-}OOC(CHOH)_3\cdot CH_2OH$
$+ HCHO + NaCl$ (1)
Xylonic acid anion

The product formaldehyde was confirmed by spot test.[11]

Results

The kinetics of oxidation of D(+)-sorbose by chloramine-T in alkaline media was investigated and it was observed that the reaction shows a marked induction period. The influence of the change of equilibrating time of sugar-alkali mixture on induction period was studied. The results show that induction period diminishes as the time of equilibrating increases and after 45 min of equilibrating time, the induction period almost disappears (Fig. 1).

The kinetics of oxidation of D(+)-sorbose by chloramine-T was followed at several initial concentrations of reactants. It was observed that the reaction follows a first order dependence in chloramine-T. Pseudo first order rate constants (k_1) in chloramine-T, calculated from the slope of the linear log-time plots, increase linearly with the increase of sugar concentration. The second order rate constants $k_2=k_1$/[Sorbose] were calculated and the average value of k_2 was ob-

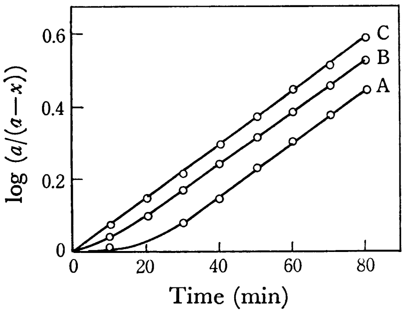


Fig. 1. First order plots at 32.5 °C.
[D(+)-sorbose]=2.0×10^{-2} M, [Chloramine-T]=2.0×10^{-3} M, [NaOH]=0.05 M, [KCl]=0.1 M and equilibrating time=0, 30, and 45 min for A, B, and C respectively.

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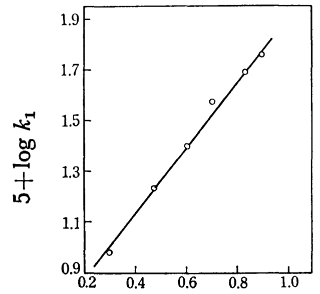


Fig. 2. Plot of log k_1 *vs.* log [D(+)-sorbose].
Conditions same as in Table 1 at [Chloramine-T]= 2.0×10^{-3} M.

tained as 13.3 l mol^{-1} s^{-1} (Table 1). The slope of the linear plot of log k_1 *vs.* log [D(+)-sorbose] (Fig. 2) was found to be unity which establishes a first order dependence in sugar concentration.

TABLE 1. EFFECT OF REACTANTS' CONCENTRATION ON RATE CONSTANTS[a)]

10^3[Chloramine-T] M	10^2[D(+)-sorbose] M	$k_1\times10^5$ s^{-1}	$k_2\times10^3$ l mol^{-1} s^{-1}
2.0	2.0	28.0	—
2.4	2.0	27.8	—
2.8	2.0	26.9	—
3.2	2.0	26.0	—
2.0	1.0	13.2	13.2
2.0	1.3	17.8	12.9
2.0	1.6	22.5	14.1
2.0	2.5	33.8	13.5
2.0	3.0	39.1	13.0

a) In presence of 0.05 M NaOH, equilibrating time=45 min and temp.=32.5 °C.

The kinetic investigations were carried out at several initial concentrations of hydroxide ions at constant ionic strength (μ=0.1 M). It was observed that the rate of oxidation of D(+)-sorbose is highly susceptible to change in alkali concentration. The order of the reaction in hydroxide ion was calculated from the slope of the plot of log k_1 *vs.* log [OH$^-$] (Fig. 3) as 1.3 for the oxidation of sorbose by chloramine-T.

The influence of neutral salts *viz.* NaClO$_4$ and KCl was investigated (Table 2). The results show that this reaction exhibits a positive salt effect.

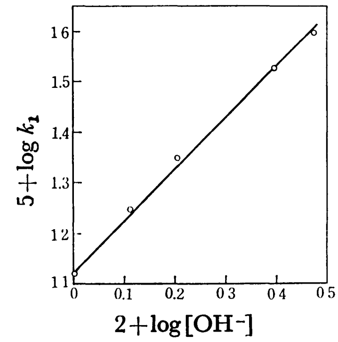


Fig. 3. Plot of log k_1 *vs.* log [OH$^-$] at 32.5 °C.
[D(+)-sorbose]=2.0×10^{-2} M, [Chloramine-T]=2.0×10^{-3} M, equilibrating time 45 min and μ=0.1 M.

TABLE 2. EFFECT OF NEUTRAL SALTS ON THE REACTION RATES[a)]

μ M	$k_1\times10^5$ s^{-1} NaClO$_4$	$k_1\times10^5$ s^{-1} KCl
0.05	30.9	30.0
0.10	38.1	37.3
0.20	46.1	44.1
0.35	52.6	56.4
0.50	66.8	—

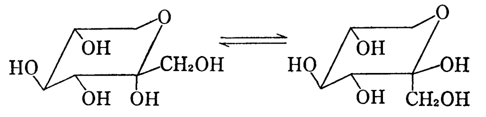
a) [Chloramine-T]=2.0×10^{-3} M, [D(+)-sorbose]= 2.0×10^{-2} M, [NaOH]=0.05 M, equilibrating time =45 min and temp.=32.5 °C.

A negligible effect of dielectric constant of the media on the reaction rate was observed. Like the oxidation of aldoses,[8,9)] osmium (VIII) ions were found to be inactive as a catalyst on the rate of oxidation of ketose by chloramine-T.

The effect of temperature was quite marked on the rate constants. The values of energy of activation, frequency factor and entropy of activation were obtained as 28.2 kcal mol^{-1}, 2.90×10^{19} l mol^{-1} s^{-1} and +29.8 e.u. respectively.

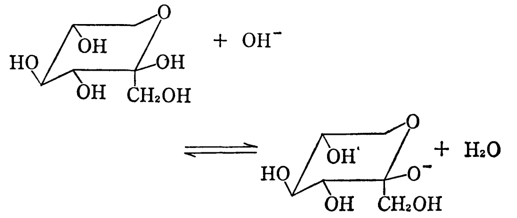
Discussion

Extensive investigations of Howorth and co-workers[12)] have shown that sugars exist as ring structures and not as open chain compounds. The most generally referred structure of sorbose is pyranose structure. It is well known that ketoses in alkaline solutions exist as anion derived from β-anomers.[13,14)] Thus the following steps are involved:



(2a)

α-D(+)-sorbopyranose β-D(+)-sorbopyranose



(2b)

anion of β-D(+)-sorbopyranose

It has been now generally accepted that β-form of the sugar is more reactive as compared to α-form. Furthermore, Hayman and Persky[14)] suggested that the anion of β-anomers is more reactive as compared to its unionised molecule.

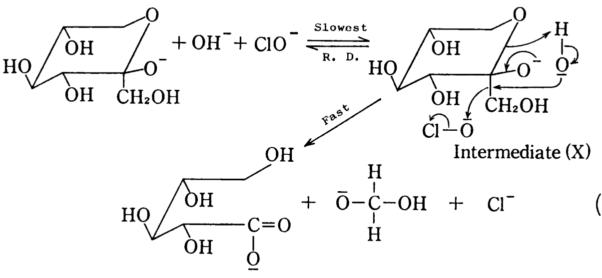
Chloramine-T (CAT) in alkaline solutions[15)] hydrolyses to *p*-chlorotoluene sulphonamide (CAT′), *p*-toluene sulphonamide (TSA) and hypochlorite ion (ClO$^-$) and the steps are given as follows:

$$\underset{\text{CAT}}{CH_3C_6H_4SO_2N\cdot NaCl} + H_2O \rightleftharpoons \underset{\text{CAT}'}{CH_3C_6H_4SO_2NHCl} + NaOH \qquad (3a)$$

$$\mathrm{CH_3C_6H_4SO_2NHCl + NaOH} \rightleftharpoons \underset{\mathrm{TSA}}{\mathrm{CH_3C_6H_4SO_2NH_2}} + \mathrm{Na^+ + ClO^-} \quad (3b)$$

From close examinations of steps (3a) and (3b) and the catalysing nature of alkali reveal the fact that any one of the hydrolysis product *viz.* CAT itself, or ClO^- would be the oxidising species. Further, a positive effect of salt clearly points out to the fact that ClO^- ion would occur in the slowest and rate determining step.

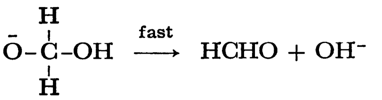
Thus, first order dependence of the reaction rate in each chloramine-T and sorbose and fractional order (1.3) dependence in hydroxide ion leads to the contention that the rate determining step involves the anion of β-D(+)-sorbopyranose, hypochlorite ion and hydroxide ion. The oxidation products were found as formaldehyde and xylonic acid and a mechanism is suggested as follows:



(4)

(5a)

Xylonic acid anion



$$\bar{O}-\underset{H}{\overset{H}{C}}-OH \xrightarrow{\text{fast}} HCHO + OH^- \quad (5b)$$

The mechanism of oxidation of D(+)-sorbopyranose (S) by chloramine-T may, therefore, be summarised as follows:

$$S + OH^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} S^- + H_2O \quad \text{slow} \qquad (2)$$

$$CAT + H_2O \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} TSA + Na^+ + ClO^- \quad \text{fast} \qquad (3)$$

$$S^- + ClO^- + OH^- \xrightarrow{k_5} \text{Intermediate (X)} \quad \text{slowest and R.D.} \qquad (4)$$

$$X \xrightarrow{k_6} \text{Products} \quad \text{fast} \qquad (5)$$

In the above scheme the step (2) is also slow but not so slow as the rate determining step (4). On adding sugar to the alkali solution, the concentration of sugar anion (S^-) increases with time. After some time when S^- becomes sufficiently high, the consumption of S^- in step (4) becomes regular and steady state is achieved. The steady state in oxidation of ketose is thus not achieved instantaneously as has also been observed in the first order rate plots (Fig. 1) where there are induction period effects. As the alkali sugar mixture has been equilibrated for 45 min for these investigations, the induction period has completely vanished. It has also been experimentally observed that the induction period minimises on increasing the temperature of the reaction mixture.

Applying steady state condition to (S^-), the rate of disappearance of ClO^- is given as:

$$-\frac{d}{dt}[ClO^-] = \frac{k_3k_5[S][ClO^-][OH^-]^2}{k_{-3}[H_2O]+k_5[ClO^-][OH^-]} \qquad (6)$$

In highly alkaline solution, ClO^- may be taken as CAT and thus Eq. (6) becomes

$$-\frac{d}{dt}[CAT] = \frac{k_3k_5[S][CAT][OH^-]^2}{k_{-3}[H_2O]+k_5[CAT][OH^-]} \qquad (7)$$

The derived Eq. (7) predicts first order dependence in both chloramine-T and sugar and a fractional order in hydroxide ion concentration. At very low concentration of alkali *i.e.* $k_{-3}[H_2O] \gg k_5[CAT][OH^-]$, the order in OH^- would be 2 and at very high concentration of alkali when $k_{-3}[H_2O] \ll k_5[CAT][OH^-]$, the dependence of the reaction rate on alkali would be unity. At the experimental conditions, however, both the extreme conditions are not achieved and thus the reaction shows a fractional order dependence in $[OH^-]$ ion being 1.3. Further from Eq. (7), the rate constant should decrease on increasing the chloramine-T concentration which has also been observed experimentally (Table 1).

A positive salt effect also confirms the rate controlling step (4). Since the rate determining step involves three similarly charged ions and, therefore, a high energy of activation value is expected and this is in agreement with the high experimental value observed *viz.* 28.2 kcal mol^{-1}.

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